CH_4 conversion in nanosecond pulsed plasma: Is it pyrolysis?

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Abstract: In this contribution, we elucidate the importance of plasma-initiated conversion of CH_4 in nanosecond (ns) pulsed plasmas versus thermal pyrolysis, using a chemical kinetics 0D model. The electron density, reduced electric field and gas temperature exhibit pulsed behavior in the model. A detailed reaction mechanism analysis shows the importance of electron-impact driven dissociations over thermal pathways when the gas temperature is below 1300 K.

1. Introduction

Methane (CH_4) is the second largest contributor to global warming [1], hence there is a growing focus on converting CH_4 into value-added products, such as H_2, C_2H_2, C_2H_4 and solid carbon. Among current CH_4 reforming technologies, plasma technology shows strong potential due to its direct and rapid activation of gas phase molecules by electron impact dissociation, electronic and vibrational excitation, etc. Ns-pulsed plasmas are of particular interest because they can give rise to strong non-equilibrium that enables CH_4 conversion at lower gas temperature than required for thermal conversion (1300 K) [2].

Therefore, we investigate here the CH_4 conversion mechanism at different pressures in ns-pulsed plasmas using a kinetic modelling approach. The reaction pathways are elucidated, as well as the role of vibrational excitation, and the importance of thermal conversion vs. electron-impact driven plasma conversion.

2. Methods

We obtained insights into the underlying plasma chemistry by developing a zero-dimensional kinetic model that was constructed by using the Zero-Dimensional Plasma Kinetics (ZDPlasKin) solver with integrated BOLSIG+ solver. The chemistry set consists of 76 species, including neutral molecules up to four carbon atoms, various ions, radicals and (vibrationally and electronically) excited species, interacting by 4404 reactions. The ns pulses of ca. 12 ns duration were introduced as a function of time by using symmetrical triangular pulses, matching the pulse energy and duration with experimental data obtained in our previous study [3]. Further input data obtained from the same experimental study consists of temporal gas temperature (T_{gas}) profiles. We validated the model by comparing with the stable products output from gas chromatography experiments and with electron density measurements (Stark broadening of H_α emission line).

3. Results and Discussion

Traditionally, CH_4 pyrolysis, $CH_4 \rightarrow 2\ H_2 + C_{(s)}$, is viewed as a thermally driven process. However, the high power densities applied with ns plasmas (ca. 2 MW per pulse) create large electric fields (E/N = 500 – 1000 Td), which in turn elevate the electron temperature (5 – 8 eV), potentially enabling electron-impact driven CH_4 conversion. Thus, the question arises: is plasma able to convert CH_4 or is the warm afterglow the driving factor? To answer this question, we have modelled CH_4 reforming under three conditions: (1) Plasma power + thermal (ns pulse + T_{gas} profile), (2) Plasma power only (ns pulse with T_{gas} = 293 K), and (3) Thermal only (T_{gas} profile, but no input power) (see Figure 1). At 0.5 bar, thermal conversion dominates because a high plasma-generated T_{gas} (> 2000 K) is maintained for a relatively long time (ca. 5 µs). At 1 bar and above, however, T_{gas} does not exceed the threshold for thermal conversion (1300 K) long enough to promote any significant conversion. Thus, all CH_4 conversion above 1 bar originates from electron-impact dissociation. The model shows that this pathway proceeds over intermediary radicals such as CH_3 and H, and the CH_4^+ ion, to yield a preferred formation of C_2H_2 and C_2H_4.

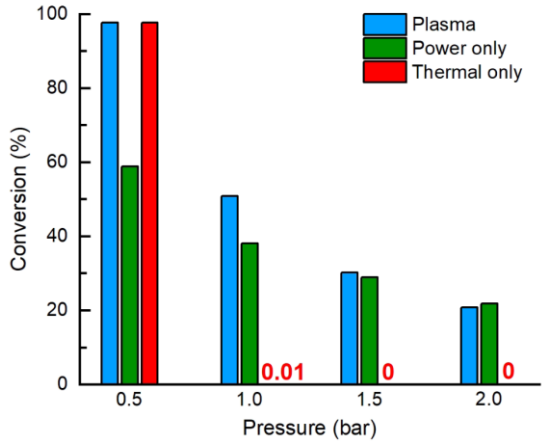

Fig. 1. Conversion vs. pressure for simulations with only power density profiles (green), only gas temperature profiles (red) and both (blue).

4. Conclusion

We have modelled a ns-pulsed plasma, using experimental data as input (T_{gas} and pulse characteristics), and we validated the model with experiments (product selectivities). We have elucidated the pathways of CH_4 conversion driven by ns-pulsed plasma at different pressures, showing the significant role of electron-impact driven CH_4 conversion when the gas temperature is lower than 1300 K.

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References

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